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INFLUENCE OF SOME FACTORS UPON HYDRIDING AND VARIATION OF PROPERTIES OF ZIRCONIUM ALLOY WITH 1 % Nb USED FOR FUEL ELEMENT CLADDING IN WATER – MODERATED WATER-COOLED POWER REACTORS

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I. Introduction

In recent years the scientists of many countries pay considerable attention to the problems of zirconium corrosion and hydriding.

The basic problem to be solved is determination of service life of zirconium alloy claddings of fuel elements and pipes operating under pressure in water-moderated water-cooled power reactors. There are many publications on this problem (I - 9).

These publications contain a lot of interesting experimental data and some theoretical concepts relating to the influence of numerous factors, such as chemical and phase composition of alloys, temperature of test, extent of irradiation, and others, upon kinetics of oxidation and hydriding resulting in variation of zirconium alloy properties.

These investigations along with the experience in operation of reactors have considerably extended our knowledge about the service life of the zirconium alloys. At the same time it should be emphasized that the problem of the service life of the zirconium alloys employed in power reactors has not been solved yet. In this connection, it is worth while mentioning the paper published in 1963 (9) concerning the effect of stresses upon distribution of the precipitated zirconium hydrides. We consider this factor to be very significant but it should be noted that this aspect of zirconium alloy durability has not been sufficiently studied.

The present paper contains some results of experimental studies devoted to the effect of preliminary hydriding and subsequent irradiation upon the mechanical properties and microstructure of specimens and fuel element claddings made of zirconium alloy with I % Nb; the data are cited concerning the influence of the amount of stresses upon orientation of hydrides in zirconium alloys with I and 2.5 % Nb.

II. Influence of Preliminary Hydriding
Upon Mechanical Properties and Corrosion Behaviour
Of Zirconium Alloys With I % Nb

To determine the influence of hydrogen upon mechanical properties of the zirconium alloy, the specimens were hydrided by means of gas saturation in the apparatus described earlier (8) at 600°C and then slowly cooled at the rate of 4°/ min.

The typical structures of the alloy after hydriding are presented in Fig.I. Hydriding of the alloy in the ustressed condition was accompanied by formation of hydride stringers located as a rule in random or sometimes in the direction of the previous deformation.

Initially the alloy contained 0.002 wt % H[x]. The specimens were hydrided to the various hydrogen contents. The specimens were irradiated in the Reactor for Physical and Technical Investigations in water loop (water temperature of 290°C, pressure of IOO atm) for 4000 hours till the integrated flux of $I.5 \cdot 10^{20} n/cm^2$ [xx] was obtained; in dry channel at $I30^\circ$C-till the integrated flux of $3.5 \cdot 10^{20} n/cm^2$ was obtained. Simultaneously the control specimens were examined in the non-irradiated portion of the water loop circuit at the same parameters of water for 4000 hours.

The results of the tensile tests are presented in Fig.2.

The test results show that with the increase of hydrogen content up to 0,08% the ultimate strength and yield point[xxx] of the non-irradiated specimens increase the most considerably, and the relative

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[x] Here and below hydrogen contents are indicated in per cents by weight.

[xx] Here and below the integrated fluxes are given for the neutrons whose energy exceeds I Mev.

[xxx] 0,2% offset.

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elongation of the specimens mostly drops at the same content of hydrogen. The same phenomena are observed in the non-irradiated specimens held in water flow (290°C and 100 atm) for 4000 hours. (curves 2). Irradiation increses the ultimate strength and yield point and reduces the relative elongation for all the specimens. In this case the effect of the hydrogen content diminishes.

The tensile tests of the irradiated specimens at 350°C showed that the ultimate strength increases by 50%, and the relative elongation decreases up to 11%. More over, hydrogen contents have a little effect both on tensile strength, and relative elongation.

This may be explained, on one hand, by decrease of strength caused by high temperature and, on the other hand, by transition of hydrogen into solid solution.

Sensitivity of the alloy to stress concentration may be easily determined by notch-tensile tests.

Fig.3 shows the dependence of the notch-tensile strength ($\sigma'_{\ell n}$) to unnotched-tensile strength (σ'_{ℓ}) ratio on hydrogen content in the alloy before and after irradiation. As it may be seen, the $\sigma'_{\ell n}/\sigma'_{\ell}$ ratio decreases with increase of hydrogen content in the non-irradiated alloy. However, it is more than 1.0 all over the range of hydrogen contents. This proves that under the given test conditions normal stresses are less than cleavage strength. In case of irradiated specimens the $\sigma'_{\ell n}/\sigma'_{\ell}$ ratio is reduced more considerably and reaches 1.0 at the hydrogen content of 0.07%. With increase of integrated irradiation flux the notch sensitivity of the alloy will grow up and the $\sigma'_{\ell n}/\sigma'_{\ell}$ ratio equal to 1.0 will be obtained at lower content of hydrogen in the alloy. Thus, the notch sensitivity of the alloy is a function both of the hydrogen content and irradiation conditions.

For the impact toughness tests the specimens of 5 mm diameter with the notch 1 mm deep and notch root radius = 0,25 mm were used. In this case the impact toughness values are 3-4 times less than those obtained with Mesnager test pieces.

The results of the impact tests of the unhydrided specimens and specimens preliminary hydrided up to 0.04 and 0.1 % H are shown in fig.4. Irradiation was performed in "dry" channel at 130°C by the integrated flux of 3×10^{20} n/cm^2.

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With increase of test temperature from -80° to $+300^\circ$C impact toughness of the non-irradiated specimens with initial hydrogen content of 0.002% rises from 2 to 5 kgm/cm^2. Preliminary hydriding to 0.04 % H decreases impact toughness from 5.5 and 2 kgm/cm^2 in initial specimens to 2.5 and I kgm/cm^2, respectively. Increase of hydrogen content up to 0.I % still more reduces resistance of the alloy to impact loads.

Irradiation of the alloy with initial content of hydrogen results in reduction of impact toughness by 20-30 %. In this case transition from ductile to brittle state of the alloy is clearly pronounced. At the hydrogen content of 0.04 and 0.I % irradiation of the alloy under the specified conditions brought to further deterioration of its impact properties (at the test temperatures up to 300°C impact toughness comprises 0.5 - I.5 kgm/cm^2).

Summarizing all the experimental data cited above, a conclusion can be drawn that at irradiation up to $I0^{20}$n/cm^2 and at temperatures ranging from 20 to 350°C the hydrogen content up to 0.04 % exerts a negligible effect upon the static mechanical properties of a zirconium alloy with I % Nb. Such a content of hydrogen considerably reduces impact toughness at temperatures below 200°C. Furthe increase of hydrogen content at the same dose of irradiation considerably impairs the properties which are responsible for structural strength and reliability of the alloy.

Specimens of zirconium alloy with I % Nb containing from 0.002 to 0.I % H were tested for corrosion in the circuit of the water loop in the RPT under the following conditions: water temperature 290°C, pressure I00 atn, rate of flow 4.5 m/sec. The specimens were located both in the active portion of the circuit where they were irradiated with the integrated dose of $I.5 \cdot I0^{20}$n/cm^2 and in the inactive portion of the circuit. The total time of test under these parameters was 4000 hours. Considerable increase ($\sim$ 8 times as large) of oxidation of irradiated specimens with 0.002 % hydrogen content should be noted. At the hydrogen content of 0.02 % and more there is no conside-

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rable difference between weight gains of the irradiated and
non-irradiated specimens. With increase of hydrogen content
a certain decrease in weight gains is traced. This may be sup-
posed to be connected with deterioration of oxide film adhe-
sion which results in extensive washdown of the oxide film due
to errosion by the water stream.

Tests in static autoclaves with water temperature of $350^{\circ}C$
and pressure of 168 atm carried out for 4000 hours proved that
preliminary hydriding did not effect the amount of weight gains.

III. Study Of Test Fuel Elements With Claddings Made
Of Zirconium Alloy With 1 % Nb.

A test cluster of fuel elements with claddings of zirconium
alloy with 1 % Nb was placed into the water loop of the RPT.
The fuel element claddings were preliminary hydrided to 0.01,
0.02, 0.03, 0.04 and 0.05 % of hydrogen content. The fuel ele-
ment diameter was 10.2 mm and length, 200 mm. The cluster of
fuel elements with pellets of uranium dioxide has successfully
operated for 4000 hours in water under a pressure of 100 atm
and at cladding surface temperature of $300^{\circ}C$. The thermal load
amounted to 520 W/cm, integrated flux was $1.5 \cdot 10^{20} n/cm^2$.

After testing in the autoclave, samples for metallographic
studies and ring-shaped specimens for determination of mecha-
nical properties were cut out of the claddings. The metallo-
graphic study of the fuel element claddings proved that samples
cut out of various zones of a single element possess identi-
cal microstructure. Comparing the obtained microstructures

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with the initial one we can, however, see the change of hydride type and arrangement in the claddings tested in the reactor. Before irradiation (fig. 1.) the hydrides in the cladding microstructures had the shape of long dark stingers preferentially oriented along circumference and uniformly distributed over the cladding cross-sections. The amount of hydrides increased with increase of hydrogen content. After test in the reactor refining the hydrides occure and their distribution changed (fig. 5). As it is clearly seen on the microphotographs, the most of the hydrides displaced towards the outer less heated portion of the claddings.

The mechanical properties of claddings were checked on the ring-shaped specimens, 2.5-3.0 mm deep. These specimens were subjected to transverse   tension in a special device.

The mechanical properties of the non-irradiated ring-shaped specimens cut out of pipes containing from 0.002 to 0.06 % of hydrogen are following: ultimate strength - 28-35 kg/mm^2 and relative elongation - from 12 to 17 %.

The tensile strength of ring-shaped specimens cut out of the fuel element cladding operated in the water loop of the RPT increase by 45-85 % as compared to that of the non-irradiated ring-shaped specimens. With increase of hydrogen content from 0.002 t0 0.06 % H the ultimate strength of the alloy is reduced from 53 to 47 kg/mm^2. This reduction in strength is the result of excessive sensitivity of the irradiated alloy

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with high content of hydrogen to stress concentration.

The values of cleavage strength and their spread seem to be determined by heterogeneity of alloy structure possessing brittle hydride inclusions which serve as stress raisers. The relative elongation after irradiation decreases and ranges from 8 to 3 % depending on the hydrogen content. It should be noted that certain number of specimens failed with zero elongation.

The analysis of the test data proves that presence of highly hydrided surface layer is a determinant of the cladding ductility and load-carrying capacity.

IV. Studying Nature Of Hydriding Under Stress Of Zirconium Alloys With 1 and 2.5 % Nb.

The studies were carried out on pipes (with outer diameter of 10.2 mm, inner diameter of 8.8 mm and length of 120 mm) made of zirconium alloys with 1 and 2.5 % Nb. The pipes were filled with the required quantity of water, sealed by argon- - arc welding, and then were placed into autoclaves with water the quantity of which was quite enough to ensure the outside steam pressure of 100 atm at $400^{O}C$. The amount of water poured inside the pipe was so selected as to ensure various excessive internal pressure at the temperature of $400^{O}C$ and thus to build up the specified tensile stresses in the pipes.

In the course of tests, the pipe outer diameters were measured to determine the phenomena of creep in the transverse

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direction. The rate of creep of the alloy with 1 % Nb comprised 3.10^{-4}%/hr for 450-1000 hours. The rate of creep of the alloy with 2.5 % Nb comprised $2.4 \cdot 10^{-4}$ %/hr for 1500- - 2000 hours. The microstructures of these pipes are presented in fig. 6. In the case of two-side contact of the water steam with the pipe walls subjected to tensile stresses ranged from 1.5 kg/mm^2 to 11.8 kg/mm^2, the hydriding of the pipe walls with different orientation of precipitated hydrides took place. It is worth while mentioning that at stresses up to 3.0 kg/mm^2 hydride stringers concentrically arranged were formed in the pipes made of zirconium alloy with 1 % Nb. At stresses of 4.4 kg/mm^2 and over the stringers of hydrides were arranged in radial direction. With increase of stresses the extention of the radial hydrides in the pipe cross-sections progressively increased. In pipes made of stronger zirconium alloy with 2.5 % Nb the radially oriented hydrides were formed at the stress of 8.8 kg/cm^2 and over. For both alloys the critical stresses at which radially oriented hydrides are formed range within 0.4-0.5 of the yield strength of each alloy at the test temperature.

In accordance with spectographic analysis results, the content of hydrogen in the zirconium alloy with 1 % Nb irrespective of imposed stresses was of the order of 0.01 % after 1000 hour testing, and that of the zirconium alloy with 2.5 % Nb, 0.02 % after 2000 hour testing.

Though the absolute quantity of hydrogen absorbed by pipes made of both alloys was actually the same (irrespective of imposed stresses), the influence of the hydrogen content upon

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the mechanical properties of the ring-shaped specimens was
different due to various orientation of the hydrides. The re-
sults of tensile tests of the ring-shaped specimens cut out of
pipes made of zirconium alloy with 1 % Nb after having been
corroded in steam at a temperature of $400^{\circ}C$ are presented in
fig. 7. The curves show that pipes subjected to stresses of
1.5 and 3.0 kg/mm^2 retained their initial values of elonga-
tion and strength nearly unchanged. At stresses ranging from
5.8 kg/mm^2 to 11.8 kg/mm^2 the relative elongation was reduced
by 50 % and 80 % respectively and the ultimate strength de-
creased to 28 kg/mm^2. This reduction in ductility and strength
is explained by structural piculiarities of hydride arrange-
ment in the pipe cross-sections.

The similar test was carried out on pipes made of zirco-
nium alloy with 1 % Nb which were hydrided at the hydrogen
temperature of $500^{\circ}C$ and at the pressure of 600 mm Hg. The ten-
sile stress in the pipe wall during hydriding was equal to
2.5 kg/mm^2. The specimen was allowed to absorb the required
quantity of hydrogen (to ensure hydrogen content of 0.02 %)
for 3-5 min at a temperature of 500°. After hydriding, the spe-
cimen was held for 3 hours (without hydrogen) and then was
cooled at a rate of 4^{0}/sec. At the metallographic examination
radially oriented hydrides extending from the surface to cer-
tain depth, can be clearly seen.

The stress of 2.5 kg/mm^2 comprises 0.4-0.5 of this alloy
yield point at the $500^{\circ}C$.

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These tests prove that formation of radially oriented
hydrides is a function of values of the tensile stress and
does not depend upon the methods of hydriding. Even at the
hydrogen content of 0.01 % with radially oriented hydrides
the pipe properties are sharply impaired; that proves the pa-
ramount importance of the values of tensile stress when using
zirconium alloys in water-moderated water-cooled power reac-
tors. On all other conditions being equal, preference should
be given to the zirconium alloys possessing high yield point
as in this case the value of the allowable hydriding stress
will be higher and reliability of operation will corresponding-
ly increase.

The allowable hydriding stress of the alloy is the maxi-
mum tensile stress at which radial orientation of the hydrides
under the specified service conditions does not yet occur.
Evidently, it is to be taken into account along with other
parameters in designing zirconium alloy claddings for fuel
elements or zirconium alloy pipes for service under pressure.

V. Metallographic Study Of Different Rod-Type
Fuel Element Clusters.

The state of the material of fuel element claddings tested
in the reactor was metallographically examined. The list of
fuel element clusters together with service conditions in
the reactor are given in table 1. The metallographic exami-
nations were performed both on the clusters which successfully

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failed. In both cases hydriding of the claddings was observed in more of less extent. Fig. 8 shows the microstructures of claddings of the clusters Nos 1 and 2. The microphotographs show that the hydrides are arranged both on the circumference and radially in the form of small dark stringers. In both clusters the fuel element claddings failed during tests in the reactor. Fig. 8-3 shows that in the zone of fracture the hydrides are oriented radially. The claddings of clusters Nos 3 and 4 contain a very negligible amount of hydrides. The microstructures of claddings of cluster No 5 are shown in fig. 9.

Fig. 10. shows the microstructures of the samples cut out of one of the fuel element clusters of the first charge of the "LENIN" ice-breaker reactor. The microphotographs reveal presence of hydride phase in some areas of the claddings. The ring-shaped specimens cut out of the fuel element claddings were subjected to mechanical tests which proved that their strength increased by 40 % and the relative elongation decreased by 60 % as compared to the non-irradiated specimens. This means that even after operation in the reactor for 3 years the fuel element can remain serviceable.

VI. Conclusion.

Numerous experimental data published now in many countries on corrosion and hydriding of zirconium alloys, a lot of water loop tests carried out, and extensive experience in the field of employment of fuel elements with zirconium alloy claddings

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in power reactor prove that in certain conditions these alloys possess high operational reliability. At the same time the behaviour of zirconium alloys was not satisfactory in some cases. Many causes of these failures have been already revealed. However we suppose that up to recent time the effect of stresses on the hydriding processes was studied very little and therefore was not taken into account in practice properly. Now it is clear that this factor effects to a certain extent on the operational reliability of the zirconium alloys, therefore firstly this problem must be studied more thoroughly and, secondly, this factor should be strictly taken into consideration while designing reactors.

Table 1.

Test Conditions Of Clusters Of Rod – Type Fuel Elements With Claddings Of Zr + 1 % Nb Alloy

| Cluster No. | Test conditions | | | | |
	Cladding surface temperature, $^{\circ}$C	Thermal load, W/cm	Time of test, h	Burn-out, mg.W.d/t	Neutron flux[x] x 10^{20}
1.	310	297	3600	7000	1.3
2.	320	297	6900	13400	2.5
3.	350	164	9900	45000	5.3
4.	300	186	13500	20000	3.4
5.	300	520	6300	1400	2.3

x) Fast neutron flux comprises 30 % of the thermal neutron flux.

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Bibliography

1. D.L. Douglase, Corrosion v. 17, No. 12, 1961.

2. J. Boulton, Corrosion of Reactor Materials, v. 2, p. 133
   JAEA Vienna, 1962.

3. S.B. Dalgaard, ibid, p. 159.

4. R.C. Asher, B Cox, ibid, p. 209.

5. A.A. Kiselev and oths, ibid, p. 67.

6. H.H. Klepfer, Journal of Nuclear Mat., v. 9, No. 1,
   p. 65-84, 1963.

7. E.C.W. Perryman and oths, Journ. Brit. Nucl. En. Soc.,
   v. 1, No. 4, 1962.

8. R.S. Ambartsumyan and oths, Proceedings of Second Interna-
   tional Conference On Peaceful Use Of Atomic Energy (Geneva),
   v. 3, p. 486.

9. M.R. Louthan and R.P. Marshall, Journal of Nuclear Mat.,
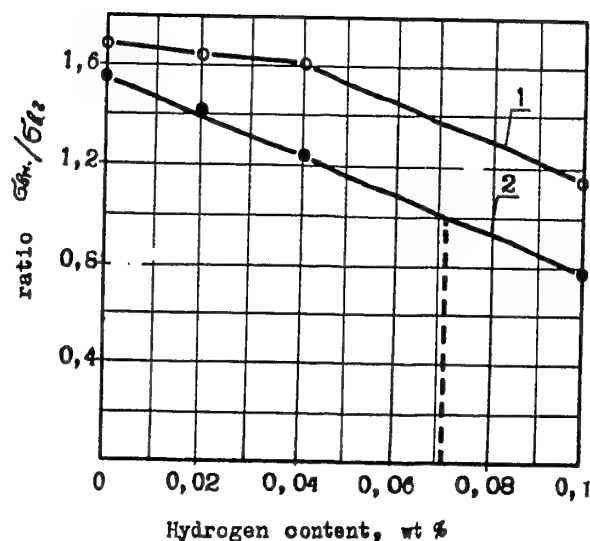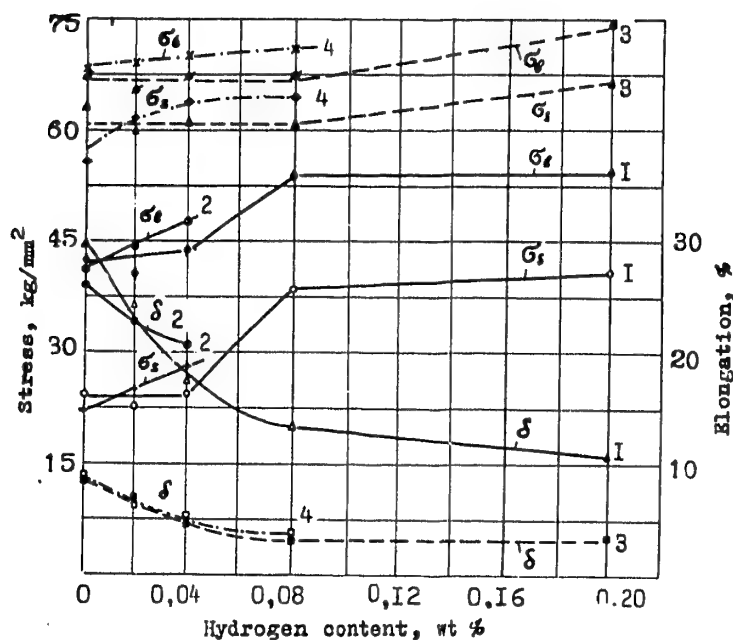   v. 9, No. 2, p. 170, 1963.
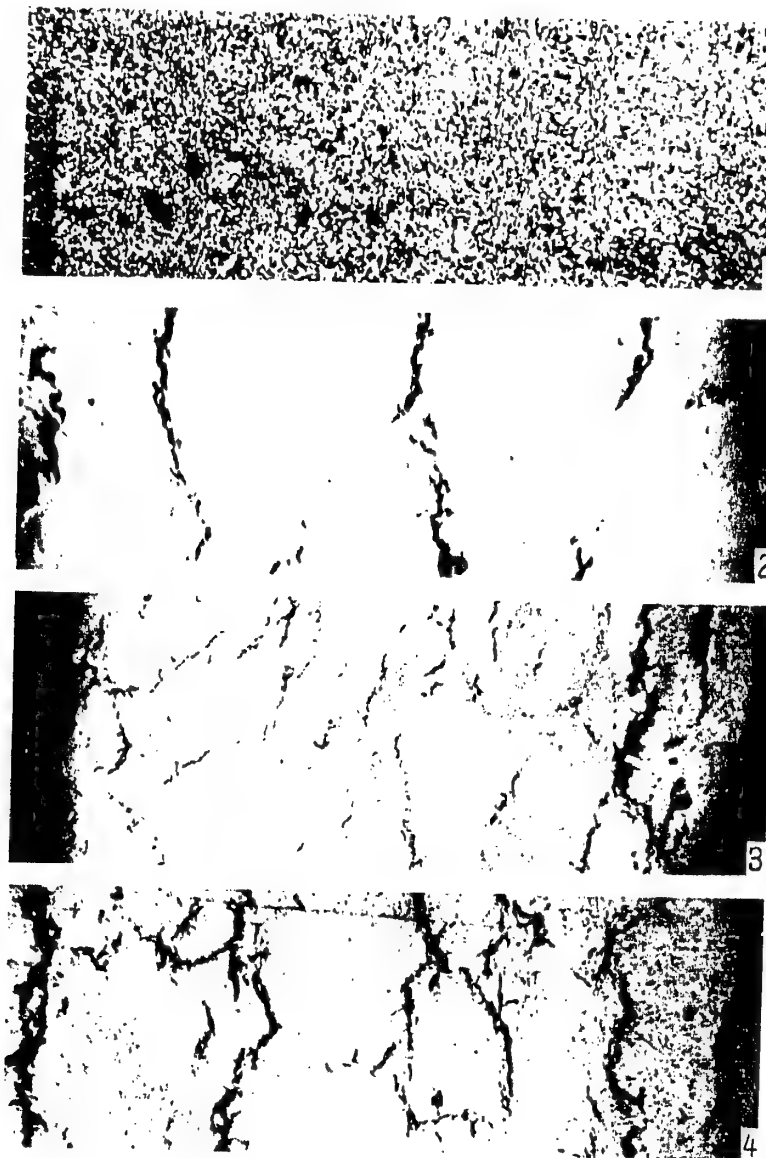
Fig. 1. Microstructures of pipes with various content of
hydrogen in alloy before irradiation.   x 200.

    1. Initial state (annealing at 700°C for 30 min) -
       - 0.002 % H.

    2. Alloy with 0.02 % H.

    3. Alloy with 0.04 % H.

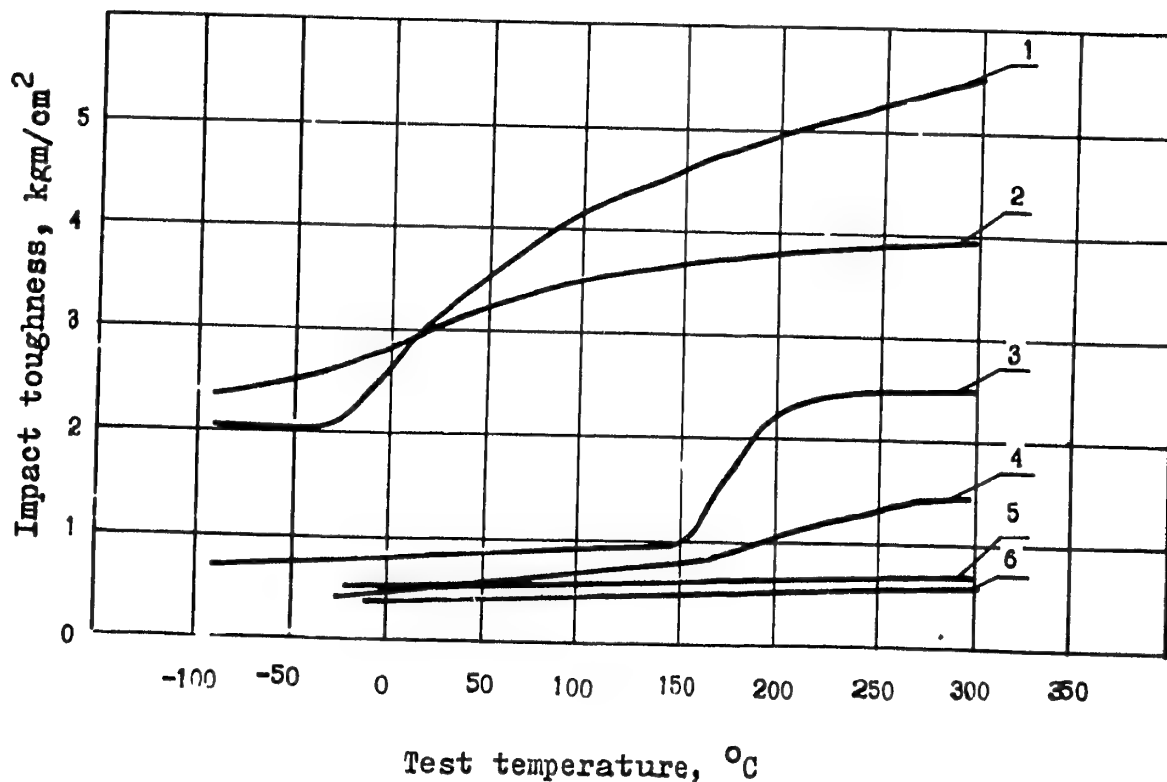   4. Alloy with 0.06 % H.

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Fig. 2. Influence of hydriding and irradiation on alloy
strength and ductility. Temperature of test 20°C.

    1. non-irradiated.

    2. non-irradiated held in water at 290°C for 4000 hours.

    3. irradiated by the flux of $3.5 \times 10^{20} n/cm^2$, 130°C.

    4. irradiated by the flux of $1.5 \times 10^{20} n/cm^2$, 290°C.

Fig. 3. Influence of hydriding on notch-tensile strength/ten-
sile strength ratio $\dfrac{\sigma_{\ell_H}}{\sigma_{\ell_s}}$

    1. non-irradiated

    2. irradiated with dose of $5 \times 10^{19} n/cm^2$, at 135°C.

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Fig. 4. Effect of the test temperature upon impact properties
of the alloy. The specimens were irradiated by flux of
$3.0 \dot{x} 10^{20} n/cm^2$, at $125^{\circ}C$.

1. Alloy with the initial   1) before irradiation
   hydrogen content   2) after irradiation

2. Alloy with 0.04; H   3) before irradiation
                                 4) after irradiation

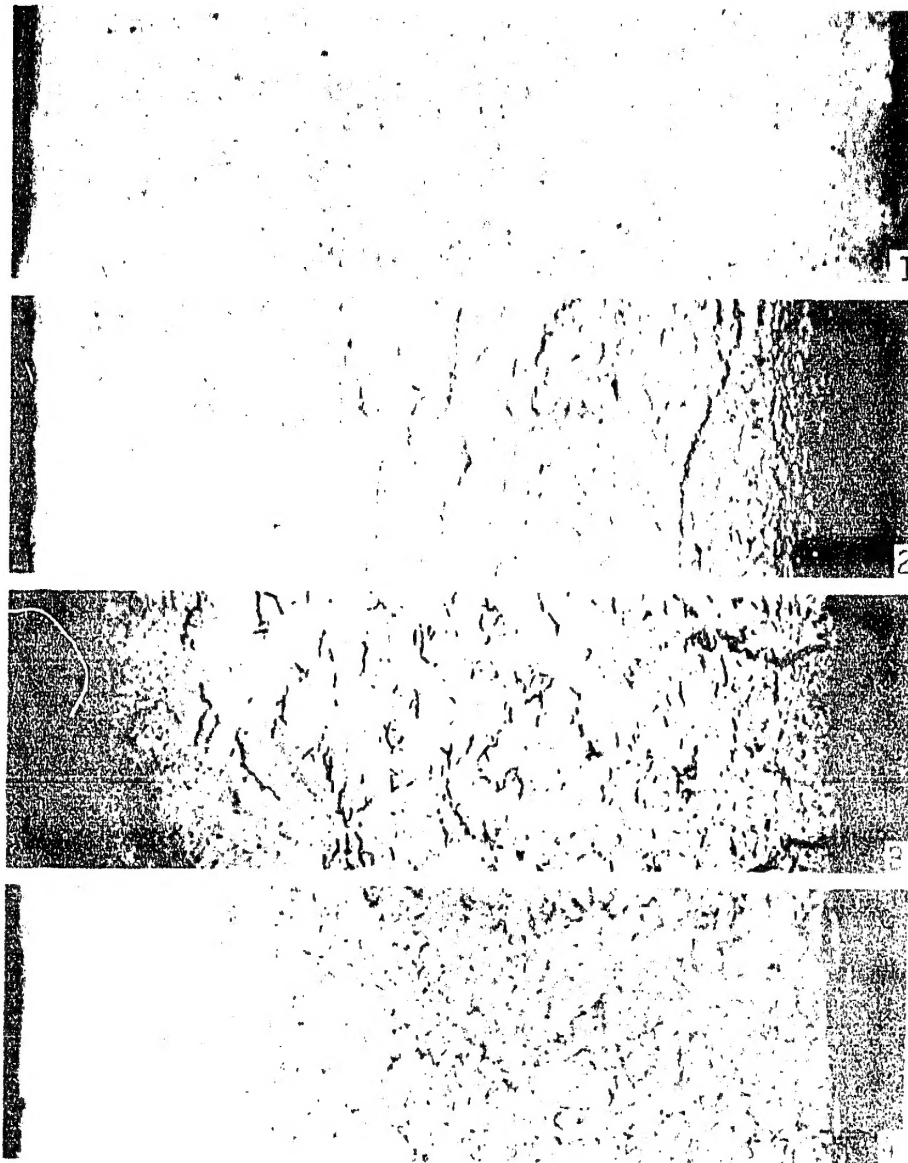3. Alloy with 0.1 % H   5) before irradiation
                                 6) after irradiation

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Fig. 5. Microstructure of fuel element claddings after
operation in reactor.   x 200.
Right—the outer surface of the cladding .
1. Alloy with 0.002 wt.% H.
2. 0.02 wt. % H.
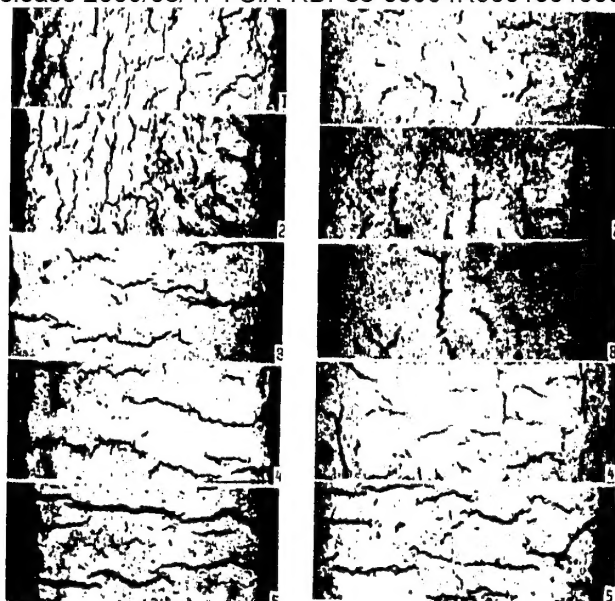3. 0.04 wt. % H.
4. 0.06 wt. % H.

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Fig. 6. Microstructures of pipes made of zirconium alloy with
1 % Nb after testing them in steam at 400°C, for 1000
hours and those of the alloy with 2.5% Nb after testing
in steam at 400°C for 2000 hours.   x 115.
                    Right - the outer surface of the pipes.

Alloy with 1% Nb: Alloy with 2.5% Nb:

1. stress of 1.5-1.0$^{x)}$kg/mm^2 1. stress of 1,5-0.3$^{x)}$kg/mm^2

2. stress of 3.0-2.4 kg/mm^2 2. stress of 4.4-3.5 kg/mm^2

3. stress of 4.4-3.9 kg/mm^2 3. stress of 5.9-5.3 kg/mm^2

4. stress of 5.9-5.5 kg/mm^2 4. stress of 8.8-8.3 kg/mm^2

5. stress of 11.8-11.0 kg/mm^2 5. stress of 11.8-11.5 kg/mm^2

x) Stress is reduced due to creep strain and due to
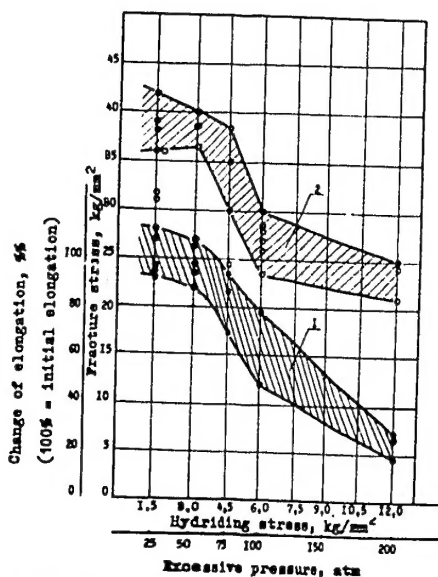   water consumption for corrosion.

Fig 7. Influence of stress corrosion on mechanical properties
of pipes made of zirconium alloy with 1% Nb which were
tested for 1000 hours in steam at 400°C. (ring-shaped
specimens were tested).

1. Change of elongation, %

2. Fracture stresses.

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Fig. 8. Microstructures of fuel element claddings of cluster

Nos 1 and 2.   x 200.

Right - the outer surface of the cladding.

1, 2, 3 - cluster No. 1; 3 - zone of fracture;
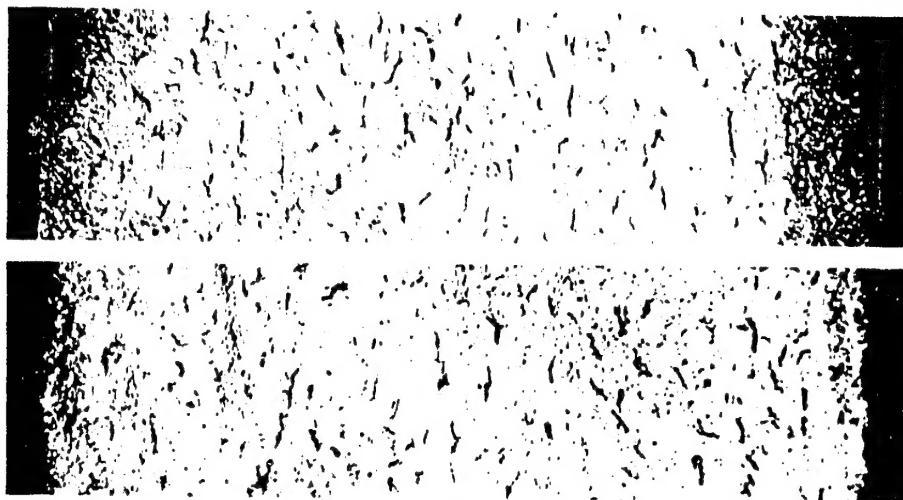
4, 5 - cluster No. 2.

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Fig. 9. Microstructures of fuel element claddings of cluster
No. 5.   x 200.
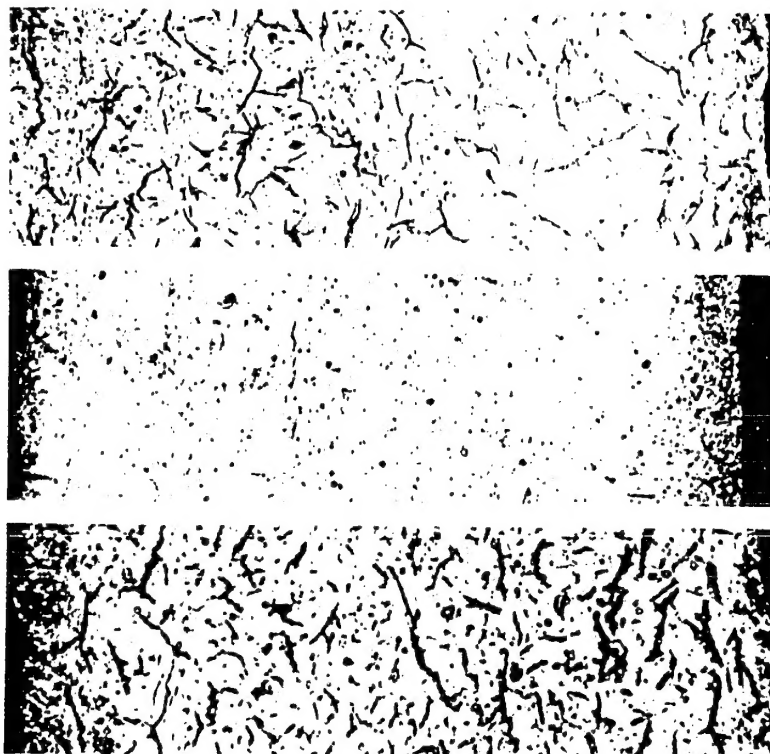Right - the outer surface of the cladding.

Fig. 10. Microstructure of fuel element cladding of one of
channels of "LENIN" ice-breaker.   x 200.
Right - the outer surface of the cladding.

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